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(54) Abstract Title  
**Determining corrosion of coated metals using leaching material**

(57) A method for testing the rate of corrosion of a coated metal sheet. The method comprises exposing a sheet of sample to a corrosive atmosphere, collecting the material leached over a period of time and subsequently determining the amount of selected ions present in the leached material. The sheet may be Zinc coated steel (with or without an extra organic coating), and selected ion may be Zn<sup>++</sup>. The sheet may be made of disc shape in which an array of (equispaced) rows and columns of perforations have been cut. The perforations may be of equal size.

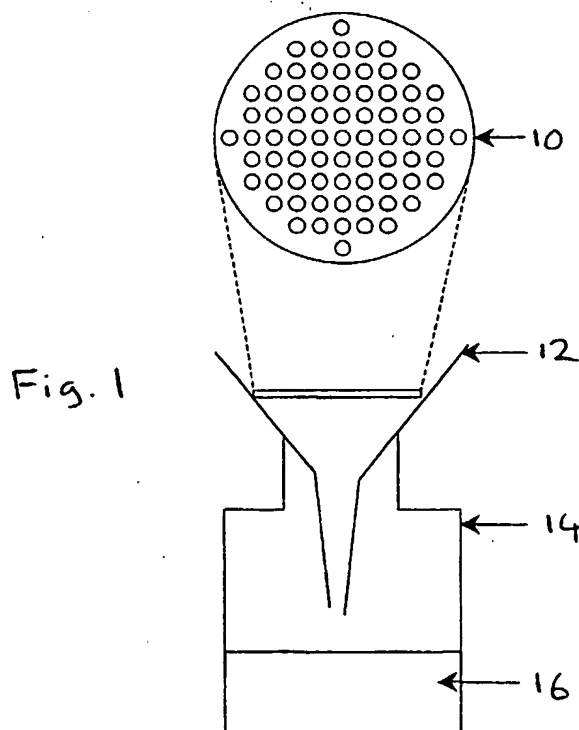
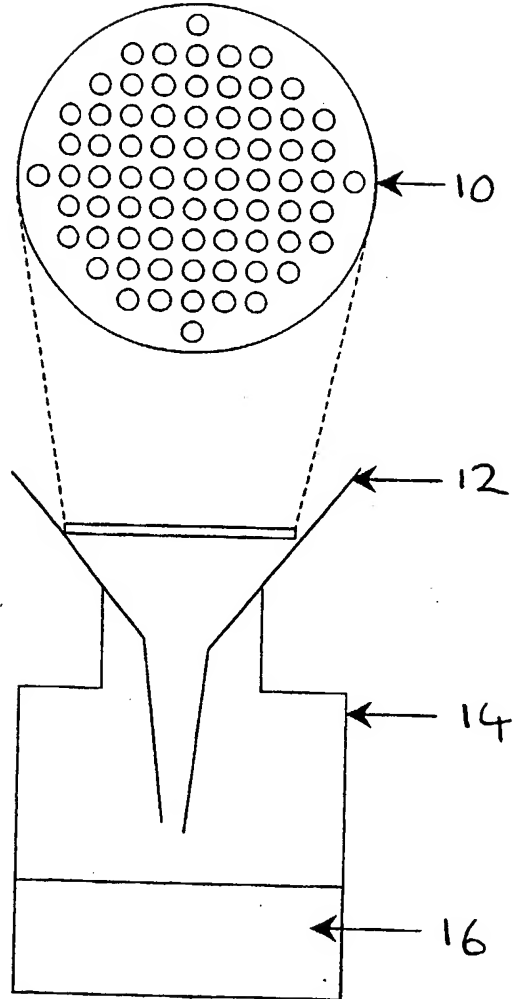


Fig. 1



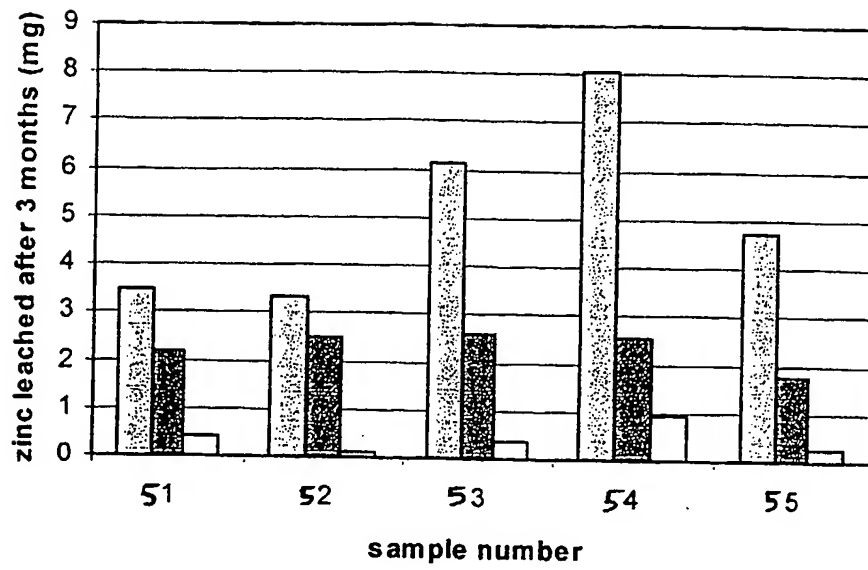


Fig. 2

Fig. 3

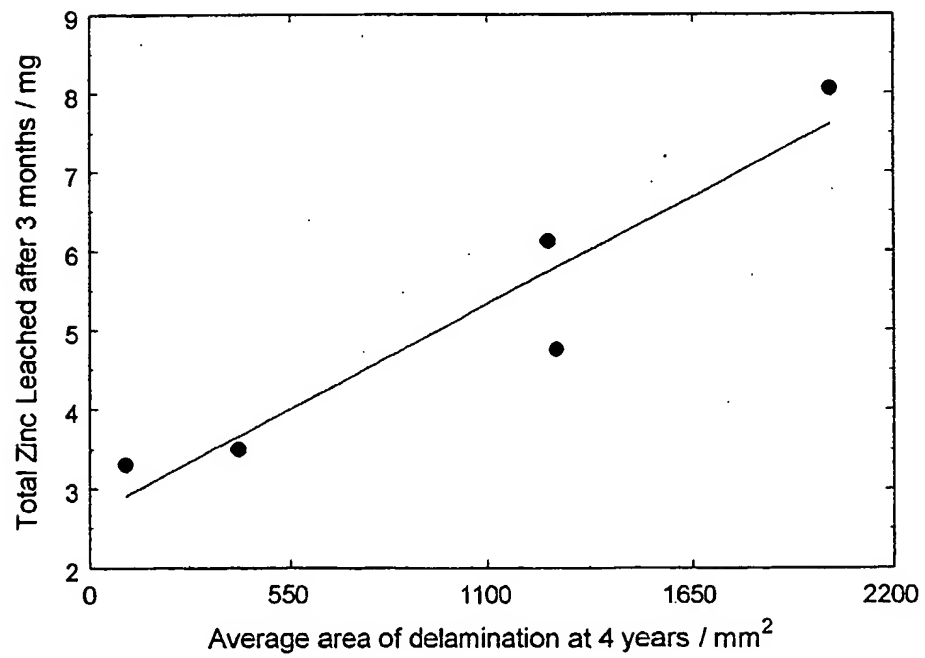


Fig. 4

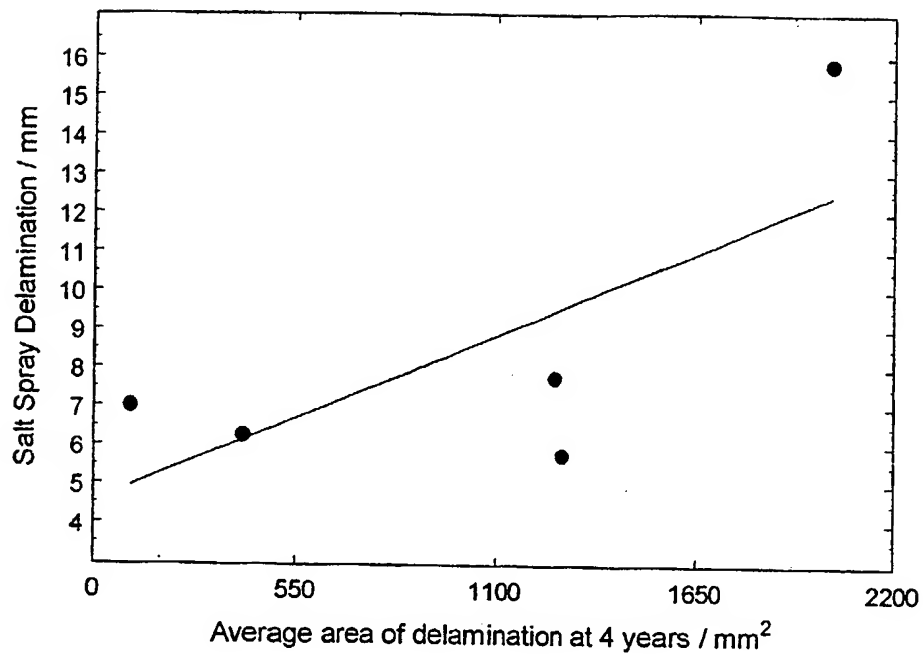
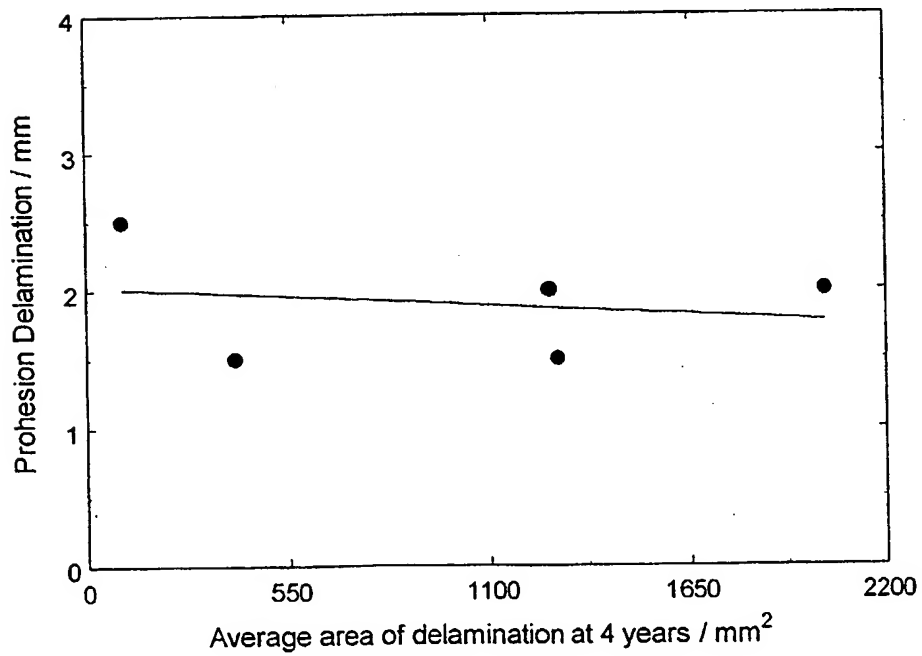


Fig. 5



Corrosion Testing

This invention is concerned with testing the rate of corrosion  
10 of a coated metal sheet and is of particular interest in the  
accelerated corrosion testing of sheet metal.

Galvanised sheet steel is of increasing importance in the  
construction industry as an inexpensive, durable material  
15 allowing rapid construction. Galvanised sheet steel is subject  
to corrosion and various types of organic coatings have been  
proposed or are being developed with a view to rendering the  
corrosion levels more acceptable. It is, however, important  
to evaluate correctly the potential corrosion performance of  
20 new coating materials and technologies. Thus, for the purposes  
of offering service lifetime estimates and guarantees (of up  
to 30 years), organically coated steel products are subjected  
to accelerated corrosion testing, and particular attention is  
paid to the performance of the material at exposed metallic cut  
25 edges.

It is highly desirable to have a testing system using an  
exposure time of say 1000 hours, or 3 months, which can  
accurately predict long term performance over several years.  
30 Known test procedures generally involve accelerating the  
corrosion reactions under laboratory conditions by the use of  
corrosive electrolytes, as in the industry standard salt spray

and Kesternich tests, or polarisation of the sample in absence of the free corrosion conditions. Whilst such testing allows  
5 for rapid evaluation of a material's performance, it does not allow for environmental effects at particular sites and the results may therefore lead to unreliable predictions. Many chromium free conversion coatings and primer systems have, for example, been rejected on the basis of poor performance in salt  
10 spray testing despite excellent external weathering performance under long term exposure conditions. Electrochemical testing such as EIS, SVET. and DC polarisation performed under laboratory conditions can provide invaluable mechanistic information on the processes of failure which can frequently  
15 enable improvements in coating technology but rarely provide accurate information on the lifetime prediction in external exposure.

We have now found that a good evaluation of long term  
20 performance of organic coated galvanised steel in a corrosive atmosphere may be achieved by analysis of electrolytes derived from a suitable test sample during exposure of the sample to the corrosive atmosphere.

25 The present invention provides a method for testing the rate of corrosion of a coated metal sheet, which method comprises exposing said sheet to a corrosive atmosphere, collecting material leached from said sheet by said atmosphere over a period of time and determining the amount of selected ions  
30 present in the material leached.

The method according to the invention is especially of interest in providing an accelerated ageing test for metal sheet materials. Preferred metal sheet materials are galvanised sheet steels, and especially those provided with organic coatings. The method described hereinafter, by way of example, employs organic coated galvanised sheet steel and preferably relies upon determination of zinc cations. Other selected ions may be determined as appropriate, and the method may be suitable for testing of sheet materials other than coated galvanised steel.

In a method according to the invention, the coated sheet is preferably in the form of a perforated sheet which is arranged to provide a large cut edge length in comparison to its area. The perforated sheet preferably has an array of perforations, typically in rows and columns. Such perforations may be substantially equispaced in such rows and/or in such columns. The perforations may be substantially equal in size.

Typically, the sample may be a disc, of for example 120 mm diameter, perforated to have an overall cut edge length of 1.5 metres whilst retaining approximately 87.5% of the substrate area. In a most preferred sample format, the disc has a regular array of 72 five mm holes.

A method according to the invention may be used to generate data concerning corrosion of the sample in a given atmosphere which data may be used to forecast corrosion behaviour of the material in the selected atmosphere over a prolonged period of time. A method according to the invention may be performed in

any suitable corrosive atmosphere. By use of the preferred sample format of coated sheet metals, which have a high cut edge length per unit area of sample, one may, with a three month period of external exposure, find an excellent correlation between the zinc cations leached from the samples of organic coated galvanised steel and the observed cut edge corrosion performance after a four year external exposure period. As mentioned, the method of the invention may be conducted in a range of appropriate weathering regimes, which enables good prediction of performance of environmentally sensitive materials in those same or similar regimes.

In order that the invention may be more clearly understood there now follows a detailed description of an exemplary method according to the invention, and three known methods by way of comparison. In the detailed description, reference is made to the accompanying drawings, in which:

Figure 1 shows a plan view of a disc-shaped test sample sheet devised for use in the present invention and a sectional diagram showing the test sample sheet in position in apparatus used to carry out the exemplary method;

Figure 2 is a block diagram showing results of tests carried out at three sites as described in Example 3;

Figure 3 is a computer generated "best fit" graph comparing results obtained in Examples 2 and 3;



Figure 4 is a computer generated "best fit" graph comparing results obtained for salt spray test in Example 1 with those of Example 2; and

Figure 5 is a computer generated "best fit" graph comparing results obtained for prohesion test in Example 1 with those of Example 2.

Samples of organic coated galvanised steel (OCS) were subjected to accelerated ageing and atmospheric ageing as described below. Five materials were used in each test as set forth in the following Table. Samples S1 and S2 were samples of hot dip galvanised steel sheet consisting of 0.7 mm gauge mild steel coated on both sides with a 20 $\mu$ m thick zinc layer (composition Zn 99.85%, Al 0.15%) supplied by British Steel Strip Products. Samples S3, S4 and S5 were samples consisting of a 0.7 mm gauge mild steel coated on both sides with a 20 $\mu$ m thick zinc / aluminium alloy layer (composition Zn 94.50%, Al 4.5% with a trace addition of Mg 0.05%). In each case, the substrate was cleaned and treated with a chromic acid rinse to aid adhesion of the subsequent polymer layers. Samples were coated asymmetrically on one side with a 200 $\mu$ m PVC plastisol layer and on the other with a 15 $\mu$ m polyester layer using different gauges of spiral wound coating bar following application of the appropriate primers (5 $\mu$ m) containing strontium chromate corrosion inhibitors. The polymers were cured by heating in an oven (Mathis Labdryer), at 300°C for 50 seconds (peak surface cure temperature of 216°C). The resulting polymer layer thicknesses were checked by magnetic induction using a Fischer Permascope.

Sample Code	Substrate	Topcoat	Primer	Pre-treatment
S1	99.85% Zn	PVC Plastisol (200 $\mu$ m) Polyester (15 $\mu$ m)	P1	PT1
S2	99.85% Zn	PVC Plastisol (200 $\mu$ m) Polyester (15 $\mu$ m)	P2	PT2
S3	95.5% Zn	PVC Plastisol (200 $\mu$ m) Polyester (15 $\mu$ m)	P2	PT2
S4	95.5% Zn	PVC Plastisol (200 $\mu$ m) Polyester (15 $\mu$ m)	P1	PT2
S5	95.5% Zn	PVC Plastisol (200 $\mu$ m) Polyester (15 $\mu$ m)	P2	PT1

#### Example 1

Comparative testing using two known methods.

Salt spray testing was carried out in accordance with standard procedures (ECCA T8; ASTM 117-73). 15 x 10 cm panels were prepared in triplicate from each of the sample materials after coating in which all but one 10cm edge of each panel were sealed with saline resistant tape. Samples were placed in the salt spray cabinet for 1,000 hours at an angle of 45 degrees with the cut edge exposed at the bottom of the sample. The electrolyte used was 5% NaCl at pH 6.5-7.2 at 40°C.

Prohesion testing was carried out according to standard procedure. Samples were placed in a prohesion chamber for 1000 hours. During this time the samples were subjected to 60 minute wet, 60 minute dry cycling and the electrolyte used was 500 ppm NaCl and 3500 ppm  $(\text{NH}_4)_2\text{SO}_4$  at pH 5.5.

## Example 2

Actual Exposure using known procedure.

Identical samples to those used in Example 1 were exposed for a period of 4 years to the atmospheres at three weathering sites in the UK. These were at Port Talbot, an industrial area with an aggressive marine component, at Torbay, a marine environment and at Blendworth, a rural area with the least corrosive atmosphere.

In this test, standard 15 x 10 cm Q-panels were prepared and exposed at 45 degrees with a single 10 cm uncoated metallic cut edge held at the bottom of the sample. After 4 years external, natural weathering exposure, the samples of OCS were recovered from the exposure sites and the total area of delamination of the PVC and polyester coatings measured using a stereo microscope. This area of delamination represents the degree of coating failure over the four year exposure period. Within the four year exposure period at the three weathering sites, delamination was only measurable on all samples from the most severe exposure environment i.e. the Port Talbot site.

## Example 3

Illustrative Process

Discs of 12 cm diameter numeral (numeral 10 in Figure 1) were cut from each of the five sample materials after coating. These coated steel discs were then punched with a regular array of 72 five mm holes as illustrated schematically in Figure 1, the punch simulating the shear action of a guillotine. This procedure gives a 12 cm disc of organically coated material an overall cut edge length of 1.5 metres whilst retaining

approximately 87.5% of the substrate area. This sample possesses a cut edge length per unit area almost 25 times greater than a standard Q-panel and three orders of magnitude greater than a standard roofing panel.

Samples were prepared and placed at the three weathering sites referred to in Example 2. Each of the coated steel discs referred to above was placed horizontally in a conical funnel (12). The run off (16) from each sample was collected in a 5 litre polyethylene jerrican (14). In each case, the samples were exposed to natural weathering exposure for three months and then the quantity of metal leachate contamination in the run off water was determined as described below.

At each site, blank samples of water were collected and analysed in order to eliminate background variations in metallic contamination in the rain water falling on the samples. All polymeric materials used were tested prior to exposure to ensure that there was no metallic leaching from anything but the samples. Plastic components were exposed to distilled water for 3 months, and then analysed as described below. This work showed that there was no detectable metallic leaching from the components used.

Metal leachates were extracted and concentrated, using an ion-exchange resin (Chelex 100 obtained from the Aldrich Chemical Company). 5 grams of the ion-exchange resin was packed in a 10cm long glass tube of 5mm internal diameter, fitted with glass tube 10 cm in length fitted with glass wool at both extremities to prevent loss of the resin beads. The leachates were forced

through the ion-exchange column at a rate of 25 ml/min. The resin was then stirred in 70 ml of sulphuric acid ( $5 \text{ mol dm}^{-3}$ ) for 60 minutes to release trapped metal cations. The resulting solution was then analysed for metals using an Atomic Emission spectrometer fitted with an Inductively Coupled Plasma torch (AE-ICP)

(Perkin Elmer Plasma 4000). The detection limit of the instrument was found to be less than 100 ppb (part per billion or  $10^{-3} \text{ mg.dm}^{-3}$ ) and thus less than 10 ppb after concentrating. This extraction technique was found to be 96 % efficient for metal recovery on standard solutions of  $\text{Zn}^{++}$  (in the concentration range 0.2-20 ppm). Results of these analyses for each sample were plotted for each of the three test sites and the results are shown in Figure 2, the first column of each triplet representing results from Port Talbot, the second representing results from Torbay and the third results from Blendworth. Results of these analyses from the Port Talbot samples were plotted against the four year delamination results for Port Talbot obtained in Example 2 and the results are shown in Figure 3.

Results of the Salt Spray delamination tests of Example 1 were plotted against the average area of delamination at four years on Port Talbot samples determined in Example 2 and the comparison is shown in Figure 4. Figure 4 shows in combination the data obtained for the metallic cut edge corrosion observed at the Port Talbot site after four years exposure and the salt spray data obtained over a 1000 hour exposure. The salt spray technique is able to predict the worst performing material, but

there is considerable error on the prediction made for the materials which represent coatings with superior corrosion resistance as evident from the scatter in the data presented in Figure 4.

Results of the prohesion tests of Example 1 were plotted against the average area of delamination at four years on Port Talbot samples determined in Example 2 and the comparison is shown in Figure 5. Since the prohesion test involves a less concentrated electrolyte and more realistic wet and dry cycling it was felt that this test might be expected to give an improved predictive performance with external exposure. The data presented in Figure 5 shows that under the conditions of exposure at a harsh marine and industrial site, the prohesion test makes incorrect predictions as to the long term exposure performance of the materials. Indeed it is clear that the data significantly underestimates the levels of corrosion.

From the comparison of the level of zinc leaching compared to the four year area of delamination shown in Figure 3, it is clear that determination of zinc leaching over 3 months provides a reasonably accurate indication of the longer term corrosion performance of the materials and provides a more realistic accelerated corrosion test approach. As noted, it is possible to obtain leaching data after 3 months in benign corrosive environment and so evaluate the likely corrosion resistance behaviour of the materials in that environment.

CLAIMS:

1. A method for testing the rate of corrosion of a coated metal sheet, which method comprises exposing said sheet to a corrosive atmosphere, collecting material leached from said sheet by said atmosphere over a period of time and determining the amount of selected ions present in the material leached.
2. A method according to claim 1, wherein the selected ions are of  $Zn^{++}$ .
3. A method according to claim 1 or 2, wherein the sheet is of zinc-coated steel.
4. A method according to claim 3, wherein the sheet has an organic coating.
5. A method according to any one of the preceding claims, wherein said sheet has an array of perforations therethrough.
6. A method according to claim 5, wherein the array of perforations comprises rows and columns of said perforations.

7. A method according to claim 6, wherein said perforations are substantially equispaced in said rows and/or in said columns.
8. A method according to any one of claims 5 to 7, wherein said perforations are substantially equal in size.
9. A method according to any one of the preceding claims, comprising the further step of obtaining forecasts of corrosion behaviour of the coated sheet in the corrosive atmosphere over a prolonged period of time.
10. A method according to any one of the preceding claims, wherein said sheet is disposed so that liquid present in said atmosphere is allowed to pass over said sample, and the liquid is collected for determination of the amount of said selected ions.





Application No: GB 0020881.9  
Claims searched: 1-10

13

Examiner: Sam Mirison  
Date of search: 11 March 2002

## Patents Act 1977 Search Report under Section 17

### Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.T): G1N (BMR)

Int Cl (Ed.7): G01N17/00, G01N 17/02

Other: ONLINE: WPI, EPODOC, JAPIO, INTERNET

### Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
A	EP 0, 342, 934 A2 (WESTINGHOUSE ELECTRIC CORP)	

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

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